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PROVISIONAL SPECIFICATION

Improvements in and relating to the Concentration and Purification of Hydrogen Peroxide by Distillation

We, B. LAPORTE LIMITED, a British Company, of Kingsway, Luton, Bedfordshire, WILLIAM STANLEY WOOD, a British Subject, of Trevesa, Glasmere Avenue, Harpenden, Hertfordshire, WILLIAM RAYMOND HOLMES, a British Subject, of 50, Grosvenor Road, Luton, Bedfordshire, and HENRY WHITTAKER, a British Subject, of Armament Research Department, Royal Arsenal, Woolwich, London, S.E.18, do hereby declare the nature of this invention to be as follows:—

This invention relates to the concentration and purification of hydrogen peroxide solutions by distillation to give a hydrogen peroxide of high concentration (which expression as used herein means hydrogen peroxide of at least 75% weight/weight concentration).

Pure and highly concentrated hydrogen peroxide solutions have been prepared on a small scale by flash vaporizing and passing the vapour into a separator to remove the impurities, and condensing the pure vapour (cf. J.A.C.S., 1920, page 2549). This peroxide was of the highest purity and of a concentration approaching 100%. A number of processes for the concentration of hydrogen peroxide on a commercial scale have been suggested but these have all been concerned with the conversion to concentrations of about 35% weight/weight from original solutions of about 3% concentration. It has not hitherto been possible to convert to concentrations approaching 100% on a large scale by distillation owing to the large losses that would be sustained and the unstable nature of the final product, due to the accumulated impurities.

It has now been found according to this invention that hydrogen peroxide up to 99% concentration and of the highest purity and stability can be made on a large scale by a continuous distillation process and with a high efficiency.

According to the present invention a process is provided for the manufacture of hydrogen peroxide of high concentration (as hereinbefore defined) which comprises distilling under reduced pressure the aqueous solution of hydrogen per-

oxide to be concentrated, said solution being of at least 27% weight/weight concentration, in a climbing film evaporator, the said solution being introduced at the base thereof, passing the product of vaporization into a separator, withdrawing hydrogen peroxide vapour as the overhead product from the separator and removing liquid hydrogen peroxide and impurities as the bottom product from the separator, passing the hydrogen peroxide vapour from the separator to a fractionating column where it is subjected to fractional distillation under reduced pressure, whilst cooling the top of the column, withdrawing concentrated liquid hydrogen peroxide as the bottom product from the fractionating column and removing water vapour as the overhead product.

If it is desired to obtain the highest possible concentration of hydrogen peroxide the liquid leaving at the bottom of the fractionating column is concentrated in a second climbing film evaporator and the products of vaporization separated in a separator, the vapour passing overhead back to the bottom of the fractionating column and the concentrated liquid hydrogen peroxide being collected in a receiver.

In order to obtain the highest degree of purity the pH value of the aqueous solution of hydrogen peroxide fed to the plant is adjusted to between pH 3 and pH 5.5 in the presence of a buffering agent, with or without the usual stabilizers so that a metal vaporizer, e.g. of aluminium, can be used and so as to ensure removal of anions.

Preferably the bottom product from the separator connected to the first climbing film evaporator is continuously returned to the inlet of the evaporator and is thus re-cycled. This re-cycling has the effect of producing a vapour containing a concentration of hydrogen peroxide which is the same as that of the feed. The process may be initiated either by introducing into the first climbing film evaporator a liquid containing at least 75% weight/weight of hydrogen peroxide or by introducing a more dilute hydro-

gen peroxide and running the climbing film evaporator until the concentration of hydrogen peroxide has built up with re-cycling of the bottom product. However, impurities gradually build up in the solution and from time to time the solution is wholly or partly run off instead of being re-cycled.

A preferred embodiment of the invention will now be described by way of example:—

The hydrogen peroxide solution to be concentrated and purified is introduced into the base of a climbing film evaporator surrounded by a heating jacket. The vaporization product passes into a separator whence the pure hydrogen peroxide vapour passes into a fractionating column. Liquid hydrogen peroxide and the impurities pass from the separator down a tube and re-enter the evaporator, thus recovering the liquid from the separator. The impurities in the hydrogen peroxide build up in the liquid circulating round through the tube and the vaporizer and from time to time all or part of this liquor is discharged from the circuit by a run-off. The pure hydrogen peroxide vapour entering the fractionating column is fractionated in known manner and a pure concentrated hydrogen peroxide leaves the bottom of the fractionating column. The top of the column is connected to a condenser and a vacuum pump so that the whole of the apparatus is under vacuum. The top of the fractionating column is provided with a water cooled coil or a water spray in known manner (cf. Specification No. 445,334) to regulate the concentration of the hydrogen peroxide leaving the bottom of the column. If the hydrogen peroxide is not required to be of the highest strength it can be run off from the bottom of the column. If, however, the pure hydrogen peroxide is to be raised to the highest concentration it runs from the bottom of the column to a second climbing film evaporator provided with a heating jacket. The hydrogen peroxide vapour from this evaporator flows into a second separator. The pure and highly concentrated hydrogen peroxide liquid leaves the separator by a tube and can be collected in a receiver. The hydrogen peroxide vapour from the separator leaves by a pipe at the top of the separator

and enters the column at the bottom to be re-fractionated.

It will be seen therefore, that the process of the present invention works with minimum loss as the products are recirculated. The only loss (apart from the slight decomposition of hydrogen peroxide) is with the periodical discharge of impurities from the first separator.

The following example, in which the apparatus referred to above was used, illustrates how the process of the invention may be carried into effect:—

The hydrogen peroxide solution introduced into the base of the first evaporator contained 28% weight/weight of H_2O_2 . A vapour containing 27.5% weight/weight of H_2O_2 passed to the fractionating column, while the liquid recirculated to the evaporator contained 73% weight/weight of H_2O_2 .

The condensing system at the top of the fractionating column was adjusted by controlling the rate of flow and temperature of the cooling water to give a hydrogen peroxide containing 73% weight/weight of H_2O_2 leaving the column. This was passed to the second vaporizer and resulted in a pure hydrogen peroxide containing 89.4% weight/weight H_2O_2 being collected. The vapour returning to the column from the second separator contained 58% weight/weight H_2O_2 . The total oxygen efficiency of the process was 94%.

The term "total oxygen efficiency of the process" means the ratio of total active oxygen fed to the still as hydrogen peroxide to the total active oxygen recovered from the still in the hydrogen peroxide solutions. Thus it is a measure of the oxygen lost by decomposition of the hydrogen peroxide solution during distillation and concentration.

The present invention thus makes possible the production of hydrogen peroxide solutions up to the highest concentrations and at the same time effects a removal of the impurities from such solutions.

Dated the 17th day of April, 1945.

ELKINGTON & FIFE,

Consulting Chemists and Chartered Patent Agents,

Bank Chambers, 329, High Holborn, London, W.C.1.

Agents for the Applicants.

COMPLETE SPECIFICATION

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50, Grosvenor Road, Luton, Bedford-
shire, and HENRY WHITTAKER, a British
5 Subject, of Armament Research Depart-
ment, Royal Arsenal, Woolwich, London,
S.E.18, do hereby declare the nature of
this invention and in what manner the
same is to be performed, to be particu-
10 larly described and ascertained in and by
the following statement:—

This invention relates to the concen-
tration and purification of hydrogen per-
oxide solutions by distillation to give a
15 hydrogen peroxide of high concentration
(which expression as used herein means
hydrogen peroxide of at least 75%
weight/weight concentration).

Pure and highly concentrated hydro-
20 gen peroxide solutions have been pre-
pared on a small scale by flash vaporis-
ing, and passing the vapour into a separ-
ator to remove the impurities, and con-
densing the pure vapour (cf. J.A.C.S.,
25 1920, page 2549). This peroxide was of
the highest purity and of a concentration
approaching 100%. Specification No.
546,530 describes a method of purifying
aqueous hydrogen peroxide produced by
30 oxidation of organic intermediates and
containing non-volatile impurities which
comprises vaporizing water and hydrogen
peroxide under a sub-atmospheric pres-
sure from an aqueous medium to which
35 the hydrogen peroxide solution to be
purified is supplied while maintaining in
said aqueous medium a substantial hydro-
gen peroxide concentration not exceeding
75% H_2O_2 by weight on said aqueous
40 medium at a rate sufficient to limit the
holding time in said aqueous medium to
a maximum of 30 minutes periodically
purging said aqueous medium to
eliminate accumulating non volatile
45 impurities, and condensing the vapours
to form purified aqueous hydrogen per-
oxide. A number of other processes
for the concentration of hydrogen per-
oxide on a commercial scale have been
50 suggested but these have all been con-
cerned with the conversion to concentra-
tions of about 35% weight/weight from
original solutions of about 3% concentra-
tion. It has not hitherto been possible
55 to convert to concentrations approaching
100% on a large scale by distillation
owing to the large losses that would be
sustained and the unstable nature of the
final product, due to the accumulated
60 impurities.

It has now been found according to
this invention that hydrogen peroxide up
to 98% concentration and of the highest
purity and stability can be made on a
65 large scale by a continuous distillation

process and with a high efficiency.

According to the present invention a
process is provided for the concentration
and purification of hydrogen peroxide
solutions to give a hydrogen peroxide of
70 high concentration (as hereinbefore
defined) which comprises distilling under
reduced pressure (as hereinafter defined)
the aqueous solution of hydrogen per-
oxide to be concentrated, in a climbing
75 film evaporator, the said solution being
introduced at a pH of between 3 and 5
at the base thereof, passing the product
of vaporization into a separator, with-
drawing hydrogen peroxide vapour as
80 the overhead product from the separator
and removing liquid hydrogen peroxide
and impurities as the bottom product
from the separator, passing the hydro-
gen peroxide vapour from the separator
85 to a fractionating column where it is
subjected to fractional distillation under
reduced pressure, whilst cooling the top
of the column, withdrawing concentrated
liquid hydrogen peroxide as the bottom
90 product from the fractionating column
and removing water vapour as the over-
head product.

If it is desired to obtain the highest
possible concentration of hydrogen per-
95 oxide the liquid leaving at the bottom
of the fractionating column is concen-
trated by a second evaporation, prefer-
ably in a second climbing film evaporator,
and the products of vaporization separ-
100 ated in a separator, the vapour passing
overhead back to the bottom of the frac-
tionating column and the concentrated
liquid hydrogen peroxide being collected
in a receiver. Alternatively, the vapour
105 passing overhead from the separator may
be passed to a second fractionating
column from which the distillate passes
to the first fractionating column and the
concentrated liquid hydrogen peroxide to
110 a receiver. However, when making
hydrogen peroxide of a concentration
greater than 90% it is necessary to work
at absolute pressure below 2" of mercury
at the point where 90% hydrogen per-
115 oxide is produced to avoid fire and
explosion risks.

In order to obtain the highest degree
of purity the pH value of the aqueous
solution of hydrogen peroxide fed to the
120 plant is adjusted between pH 3 and pH 5.5
in the presence of a buffering agent with
or without the usual stabilisers so that a
metal evaporator, e.g. of aluminium, can
be used and so as to ensure removal of
125 anions. As the pH of a concentrated
hydrogen peroxide solution is difficult to
determine it is preferable to specify this
by a titration figure. Preferably this is
less than 1.5 milliequivalents to Congo
130

Red as indicator. The term "1.5 milli-equivalents to Congo Red" means that the acidity of the hydrogen peroxide solution is equivalent to 0.0015 Normal when titrated with standard sodium hydroxide using Congo Red as indicator. For neutralisation it has been found that the preferred alkali is ammonium hydroxide.

10 Preferably the bottom product from the separator connected to the first climbing film evaporator is continuously returned to the inlet of the evaporator and is thus re-cycled. This re-cycling
15 has the effect of producing a vapour containing a concentration of hydrogen peroxide which is the same as that of the feed. The process may be initiated either by introducing into the first climbing
20 film evaporator a liquid containing at least 75% weight/weight of hydrogen peroxide or by introducing a more dilute hydrogen peroxide and running the climbing film evaporator until the con-
25 centration of hydrogen peroxide has built up with re-cycling of the bottom product. However, impurities gradually build up in the solution and from time to time the solution is wholly or partly
30 run off instead of being re-cycled. If desired, the solution can be collected from the separators and steam distilled to recover the hydrogen peroxide or utilised in any other manner.

35 The invention will now be further described with reference to the accompanying drawings, in which:—

Fig. 1 shows diagrammatically an apparatus suitable for carrying out the
40 process of the invention, and

Fig. 2 shows a modification of the apparatus of Fig. 1.

Referring to Fig. 1 of the drawings, the hydrogen peroxide solution to be
45 concentrated and purified is introduced through tube 1 controlled by valve 1a into the base of a climbing film evaporator 2 surrounded by a heating jacket 3. The vaporization product passes via tube
50 4 into a separator 5 whence the pure hydrogen peroxide vapour passes via tube 6 into a fractionating column 7. Liquid hydrogen peroxide and the impurities pass from the separator 5 down a tube 8
55 and re-enter the vaporizer 2 via reservoir 9 and tubes 10 and 11, thus recovering the liquid from the separator. The impurities in the hydrogen peroxide build up in the liquid circulating round
60 through the tubes and the vaporizer and from time to time all or part of this liquor is discharged from the circuit by a run-off 11 controlled by valve 11a. The pure hydrogen peroxide vapour entering
65 the fractionating column is fractionated

in known manner and a pure concentrated hydrogen peroxide leaves the bottom of the fractionating column by tube 12. The top of the column is connected to a condenser 13 and a vacuum pump (not shown) connected to the tube 14 so that the whole of the apparatus is under vacuum. The top of the fractionating column is provided with a water cooled coil 15 or a water spray in known manner (cf. Specification No. 445,334) to regulate the concentration of the hydrogen peroxide leaving the bottom of the column. If the hydrogen peroxide is not required to be of the highest strength it can be run off from the bottom of the column. If, however, the pure hydrogen peroxide is to be raised to the highest concentration it runs from the bottom of column to a second climbing film evaporator 16 provided with a heating jacket 17. The hydrogen peroxide vapour from this vaporizer flows by tube 18 into a second separator 19. The pure and highly concentrated hydrogen peroxide liquid leaves the separator by a tube 20 and can be collected in receivers 21. The hydrogen peroxide vapour from the separator 19 leaves by a pipe 22 at the top of the separator and enters the column
7 at the bottom to be refractionated.

Referring to Fig. 2 of the drawings, it will be seen that the apparatus is modified in that the overhead vapour from the separator 19 passes by a pipe 23 to fractionating column 24 having a reservoir 25 for supplying reflux. The distillate from the column is returned by pipe 26 to the column 7 and the liquid residue passes by tube 28 to the reservoirs 21. The liquid
105 residue from the separator 19 passes down the tube 27 and is drawn off through valve 27a.

It will be seen, therefore, that the process of the present invention works with minimum loss as the products are recirculated. The only loss (apart from the slight decomposition of hydrogen peroxide) is with the periodical discharge of impurities from the first separator.
115 The following examples, in which the apparatus referred to above was used, illustrate how the process of the invention may be carried into effect:—

1. In this example the apparatus of Fig. 1 was used. The hydrogen peroxide solution introduced into the base of the first evaporator contained 28% weight/weight of H_2O_2 . A vapour containing 27.5% weight/weight of H_2O_2 at 57° C. and a pressure of 1.7 inches of mercury absolute passed to the fractionating column, while the liquid recirculated to the evaporator contained 73% weight/weight of H_2O_2 .

The condensing system at the top of the fractionating column (the pressure at this point being 1.3 inches of mercury absolute) was adjusted by controlling the rate of flow of the cooling water, which had a temperature of 13° C. to give a hydrogen peroxide containing 73% weight/weight of H_2O_2 leaving the column at 57° C. and a pressure of 1.7 inches of mercury absolute. This was passed to the second vaporizer and resulted in a pure hydrogen peroxide containing 89.4% weight/weight H_2O_2 being collected, the temperature and pressure at the collecting point being 70° C. and 1.7 inches of mercury absolute respectively. The vapour returning to the column from the second separator contained 58% weight/weight H_2O_2 . The total oxygen efficiency of the process was 98.8%. Thus, 1.2% was lost by decomposition.

The term "total oxygen efficiency of the process" means the ratio of total active oxygen fed to the still as hydrogen peroxide to the total active oxygen recovered from the still in the hydrogen peroxide solutions. Thus it is a measure of the oxygen lost by decomposition of the hydrogen peroxide solution during distillation and concentration.

The percentage removal of the impurities from the hydrogen peroxide was as follows:—

SO_4	NO_3	P_2O_5	NH_4
99.0%	97.4%	97.5%	96.0%

the impurities in the feed and finished product both being calculated to the same hydrogen peroxide concentration. The above figures are based on the average analysis of the product for a run extending over 40 hours when the impurities in the separator had concentrated to 100 times that of the original feed solution.

2. In this example the apparatus of Fig. 2 was used. The hydrogen peroxide introduced into the base of the first evaporator contained 28% weight/weight of hydrogen peroxide. A vapour containing 27.4% weight/weight at 57° C. and a pressure of 1.7 inches of mercury absolute was passed to the first fractionating column, while the liquid recirculated to the evaporator contained 73% weight/weight of hydrogen peroxide.

The condensing system at the top of the first fractionating column was adjusted by controlling the rate of flow of the cooling water, which had a temperature of 13° C. to give a hydrogen peroxide solution containing 73% weight/weight of hydrogen peroxide leaving the column, the temperature and pressure at this point being 57° C. and 1.7 inches of mercury absolute respectively. This was

passed to the second vaporizer and gave a vapour having a pressure of 1.75 inches of mercury absolute and containing 72.5% weight/weight of hydrogen peroxide, the liquor passing back containing 90% weight/weight of hydrogen peroxide, the temperature of which was 72° C. The condensing system at the top of the second fractionating column was adjusted by controlling the rate of flow of the cooling water, which had a temperature of 13° C., to give a hydrogen peroxide solution containing 89% weight/weight of hydrogen, the temperature and pressure being 71° C. and 1.75 inches of mercury absolute respectively. The total oxygen efficiency was 98.9%. Thus, 1.1% was lost by decomposition.

The percentage removal of the impurities from the hydrogen peroxide was as follows:—

SO_4	NO_3	P_2O_5	NH_4
99.9%	97.1%	99.8%	99.2%

In this case the analysis of the purified concentrated hydrogen peroxide was as follows, the impurities being given in gm./litre:—

SO_4	NO_3	P_2O_5	NH_4
<0.003	0.008	0.001	0.007

The above figures are based on the average analysis of the products for a run extending over 90 hours when the impurities in the separator had concentrated to 110 times that of the original feed solution.

The present invention thus makes possible the production of hydrogen peroxide solutions up to the highest concentrations and at the same time effects an almost complete removal of the impurities from such solutions.

The term "reduced pressure" as used herein means a pressure not exceeding 6 inches of mercury absolute.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the concentration and purification of hydrogen peroxide solutions to give a hydrogen peroxide of high concentration (as hereinbefore defined) which comprises distilling under reduced pressure (as hereinbefore defined) the aqueous solution of hydrogen peroxide to be concentrated, in a climbing film evaporator, the said solution at a pH of between 3 and 5 being introduced at the base thereof, passing the product of vaporization into a separator, withdrawing hydrogen peroxide vapour as the overhead product from the separator and removing liquid hydrogen peroxide and impurities as the bottom product from the

separator, passing the hydrogen peroxide vapour from the separator to a fractionating column where it is subjected to fractional distillation under reduced pressure, whilst cooling the top of the column, withdrawing concentrated liquid hydrogen peroxide as the bottom product from the fractionating column and removing water vapour as the overhead product.

2. A process as claimed in Claim 1 wherein the liquid leaving at the bottom of the fractionating column is subjected to a second evaporation.

3. A process as claimed in Claim 2 wherein the products of vaporization from the second evaporation are separated in a separator, the vapour passing overhead back to the bottom of the fractionating column and the concentrated liquid hydrogen peroxide being collected in a receiver.

4. A process as claimed in Claim 2 wherein the products of vaporization from the second evaporation are separated in a separator, the vapour passing overhead from the separator is passed to a second

fractionating column from which the distillate passes to the first fractionating column and the concentrated liquid hydrogen peroxide to a receiver.

5. A process for the concentration and purification of hydrogen peroxide solutions to give hydrogen peroxide of high concentration (as hereinbefore defined) substantially as described with reference to Fig. 1 of the accompanying drawings.

6. A process for the concentration and purification of hydrogen peroxide solutions to give a hydrogen peroxide of high concentration (as hereinbefore defined) substantially as described with reference to Fig. 2 of the accompanying drawings.

7. Hydrogen peroxide of high concentration (as hereinbefore defined) when produced by the process claimed in any one of the preceding claims.

Dated the 14th day of March, 1946.

ELKINGTON & FIFE

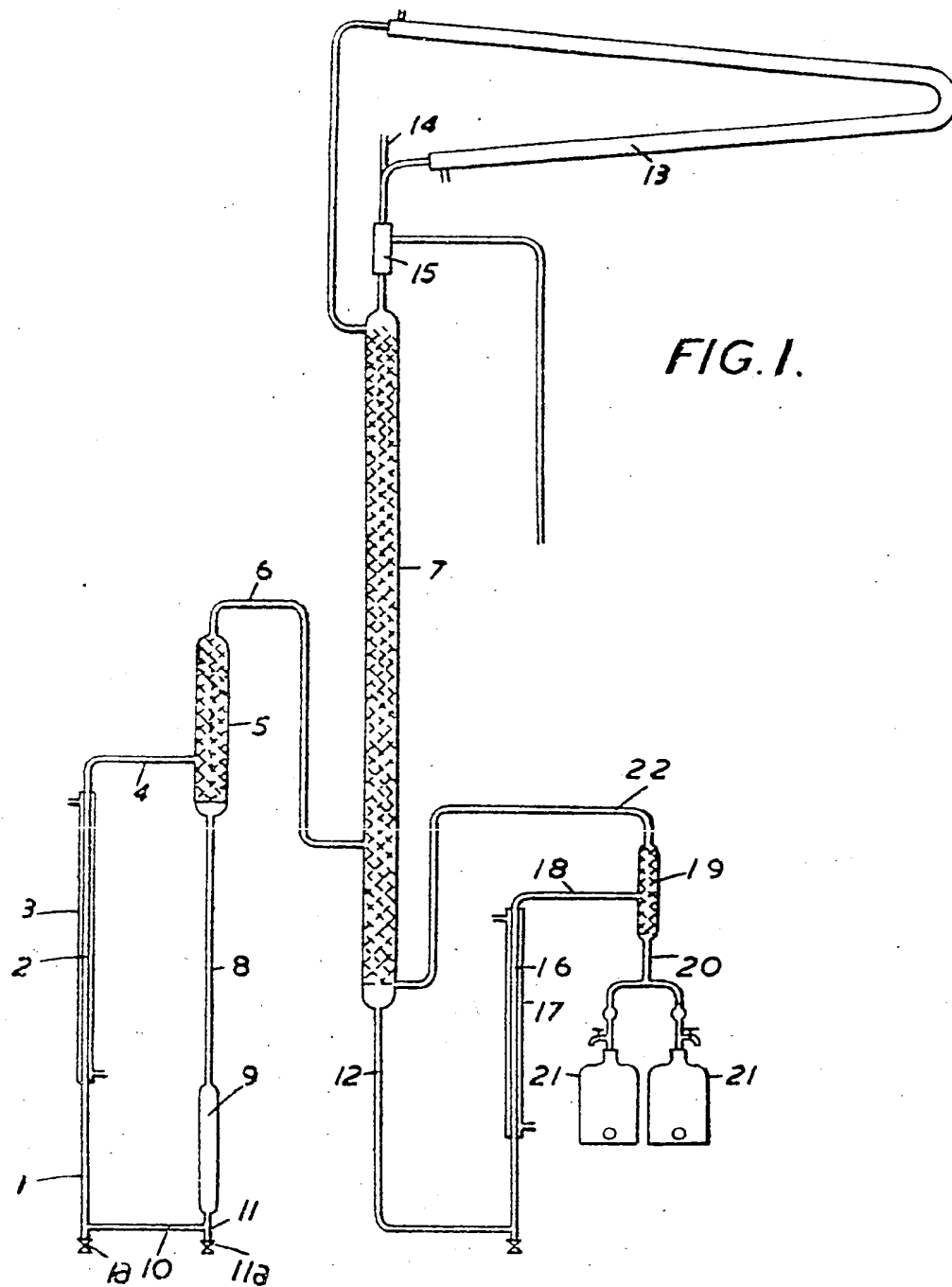
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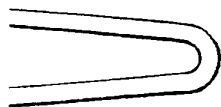
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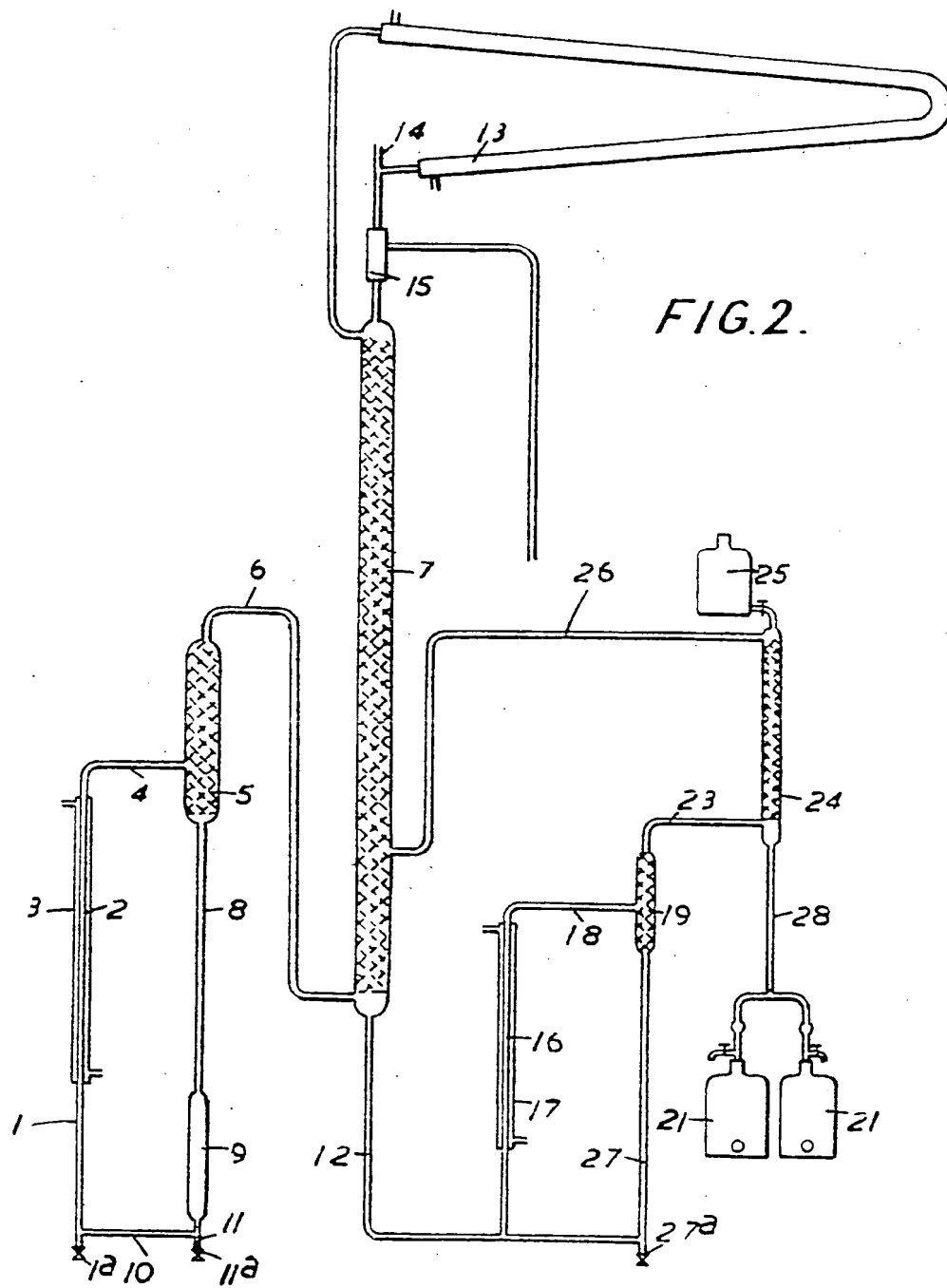


FIG. 2.